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Effect of halogen substitution on the enthalpies of solvation and hydrogen bonding of organic solutes in chlorobenzene and 1,2-dichlorobenzene derived using multi-parameter correlations

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ABSTRACT

Enthalpies of solution at infinite dilution at 298 K, $\Delta_{soln}H^{A/Solvent}$, have been measured by isothermal solution calorimetry for 43 and 72 organic solutes dissolved in chlorobenzene and 1,2-dichlorobenzene, respectively. The measured $\Delta_{soln}H^{A/Solvent}$ data, along with published $\Delta_{soln}H^{A/Solvent}$ values taken from the published literature for solutes dissolved in both chlorobenzene solvents, were converted to enthalpies of solvation, $\Delta_{solv}H^{A/Solvent}$, using standard thermodynamic equations. Abraham model correlations were developed from the experimental $\Delta_{solv}H^{A/Solvent}$ data. The best derived correlations describe the experimental gas-to-chlorobenzene and gas-to-1,2-dichlorobenzene enthalpies of solvation to within standard deviations of 1.5 kJ mol^{-1} and 1.9 kJ mol^{-1}, respectively. Enthalpies of X—H. . .π (X – O, N, and C) hydrogen bond formation of proton donor solutes (alcohols, amines, chlorinated hydrocarbons, *etc.*) with chlorobenzene and 1,2-dichlorobenzene were calculated based on the Abraham solvation equation. Obtained values are in good agreement with the results determined using conventional methods.

1. Introduction

This study continues our combined experimental and theoretical examination of gas-to-organic solvent transfer processes for nonelectrolyte solutes [1–19]. Such processes govern chemical separations by gas–liquid chromatography, measurement of solubilities and activity coefficients by inert-gas stripping methods, and the removal and pre-concentration of volatile organic solutes from aqueous analytical samples using headspace single drop microextraction methods. The latter extraction process involves two partition coefficients, the first for solute transfer to the gas phase from the aqueous solution being analyzed, and the second for solute transfer into the suspended liquid drop of the micro-extraction device. A complete understanding of the solute transfer process requires not only examining how the equilibrium partition coefficient depends on the polarity and hydrogen-bonding character of the solute and solvent molecules, but also on understanding the enthalpic effects that determine how the gas-to-organic solvent partition coefficients of the different solute-solvent combinations vary with temperature.

In previous publications [1–15] we have developed Abraham model correlations:

$$\Delta_{solv}H^{A/Solvent} = c_{h,l} + e_{h,l}\cdot\mathbf{E} + s_{h,l}\cdot\mathbf{S} + a_{h,l}\cdot\mathbf{A} + b_{h,l}\cdot\mathbf{B} + l_{h,l}\cdot\mathbf{L} \quad (1)$$

$$\Delta_{solv}H^{A/Solvent} = c_{h,v} + e_{h,v}\cdot\mathbf{E} + s_{h,v}\cdot\mathbf{S} + a_{h,v}\cdot\mathbf{A} + b_{h,v}\cdot\mathbf{B} + v_{h,v}\cdot\mathbf{V} \quad (2)$$

for mathematically describing experimental enthalpies of solvation, $\Delta_{solv}H^{A/Solvent}$, of inert gases and organic vapors dissolved in water and in a wide range of organic solvents of varying polarity and hydrogen bonding character. The organic solvents included several saturated hydrocarbons [1,2] and aromatic hydrocarbons [1,3,4], chlorinated alkanes [4–6], several primary, secondary and tertiary alcohols [7–11], two dialkyl carbonates [12], one alkyl acetate solvent [13], one dialkyl ether [13] and two cyclic ethers [6,8], as well as several miscellaneous organic solvents [9,14,15]. In each case Eqs. (1) and (2) were found to provide a reasonably accurate mathematical description of the experimental enthalpy of solvation

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